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TO
FLUORINE COMPOUNDS, ORGANIC

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Nitrogen. Nitrogen does not react with fluorine under ordinary conditions and is often used as a diluent for moderate fluorinations. However, it can be made to produce nitrogen trifluoride, NF_3 , by radiochemistry (30), glow discharge (31), or plasma (32) synthesis.

Noble Gases. Fluorine has the unique ability to react with the heavier noble gases (krypton, xenon, and radon) to form binary fluorides. With xenon at RT in uv radiation a difluoride, XeF_2 , is formed (16-18) (21,33-34). A tetrafluoride, XeF_4 , is obtained by mixing an excess of fluorine with xenon and heating to 400°C (33,35). Fluorine and xenon at 300°C under 6-6.8 MPa (60-67 atm) yield the hexafluoride, XeF_6 (36-37). Fluorine combines with radon at 400°C to yield a compound of low volatility, probably the difluoride (38). Krypton reacts with fluorine in an electric discharge at liquid air temperatures to yield the difluoride, KrF_2 (39).

Hydrogen. The reaction between fluorine and hydrogen is self-igniting and extremely energetic. It occurs spontaneously at ambient temperatures as evidenced by minor explosions which sometimes occur in fluorine-generating cells from the mixing of the H_2 and F_2 streams. The controlled high-temperature reaction of fluorine atoms (generated thermally or photolytically from fluorine gas) with hydrogen or deuterium is one of the most significant energy sources for the high power chemical laser. Over 50% of the energy released in the reaction of the hydrogen molecule with the fluorine atom appears preferentially in the vibrational energy mode of the newly formed diatomic molecules (40). On this basis, a substantial fraction of the exothermic energy of the overall hydrogen-fluorine reaction (perhaps 25%) could be released as laser radiation. Currently, the HF-DF laser is the most promising chemical laser system under development (41) (see Lasers; Hydrogen energy).

Ammonia. Ammonia (qv) reacts with excess fluorine in the vapor phase to produce N_2 , NF_3 , N_2F_2 , HF, and NH_4F . This reaction is difficult to control in the vapor phase because of the intense heat of reaction, and in some cases only N_2 and HF are produced. Nitrogen trifluoride was obtained in 6% yields in a gas-phase reaction over copper (42). Yields of ca 60% are achieved by the reaction of fluorine and ammonia in a molten ammonium acid fluoride solution (43-44).

Organic Compounds. Generally, the reaction of fluorine with organic compounds is accompanied by ignition or violent explosion. Since the heats evolved are always high, heat removal is the main problem in direct fluorination. Reactions can be moderated by dilution with large amounts of an inert gas, such as nitrogen, by reducing reaction temperatures ($\leq 78^\circ\text{C}$), or by the presence of finely divided metal packing. The latter is used in the so-called catalytic fluorination of organic vapors, originally developed in the United States (45). It takes place over a metal reactor packing such as copper gauze, metal screen, wire, chips, ribbon, or shot, which control the reaction by reducing local heating.

Saturated hydrocarbons under controlled conditions react with elemental fluorine to give perfluorocarbons, usually accompanied by some fragmentation and polymerization (46-47). The fluorination of aromatic compounds gives degradation products, polymers, unstable unsaturated compounds, or highly fluorinated cyclohexane derivatives, but no aromatic compounds. Methanol and acetone give a variety of fluorinated carbonyl compounds (48-49) (see Fluorine compounds, organic-direct fluorination).

The direct fluorination of uracil (2,4-pyrimidinedione), $\text{C}_4\text{N}_2\text{H}_4\text{O}_2$, in aqueous solution to give 5-fluorouracil (5-fluoro-2,4-pyrimidinedione), $\text{C}_4\text{N}_2\text{H}_3\text{FO}_2$, has been

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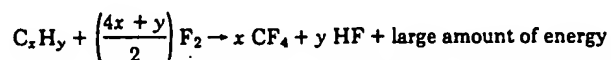
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DIRECT FLUORINATION

Organic compounds containing fluorine are well known for their special properties, especially their inertness and very low boiling points and comparatively high melting points. Binary compounds of carbon and fluorine, commonly called fluorocarbons, can be traced back to Moissan who, in 1886, discovered and isolated fluorine (1). Initial attempts at reactions between fluorine and hydrocarbons were described as similar to combustion and the reaction products contained mostly carbon tetrafluoride and hydrogen fluoride:



This reaction has often reached explosive proportions in the laboratory. In 1940–1965 several methods were devised for controlling it. Thus, for fluorination of hydrocarbons of low molecular weight at room temperature or below, yields as high as 80% of perfluorinated products have been reported together with partially fluorinated species (2–4). However, in a typical fluorination reaction involving elemental fluorine with complex hydrocarbons at elevated temperatures, appreciable cleavage of the carbon–carbon bonds occurs and the yields invariably are only a few percent.

The simplest solid fluorocarbon (5) is poly(fluoromethyldiene) -(CF)_n , CFX (MarChem), with a layered structure (see Fig. 1). It can be synthesized by the reaction of fluorine with graphite at 300–600°C and fluorine pressures up to 101 kPa (1 atm) (6–7). Other solids (C_4F , C_2F , etc) have also been reported from the reaction of F_2 with graphite (8–9). This material is a grayish to white powder of variable stoichiometry and stable up to 600°C in air. It has a very low coefficient of friction, similar to Teflon, and is an excellent lubricant which can be used up to 600°C, surpassing Teflon which softens and decomposes above 350°C (see Polytetrafluoroethylene). When -(CF)_n decomposes above 650°C, it yields mainly carbon black (finely divided soot) and the inert gas, carbon tetrafluoride (10). Thus, it can be used safely at high temperatures without any risk of poisonous gases being produced on decomposition (5,11).

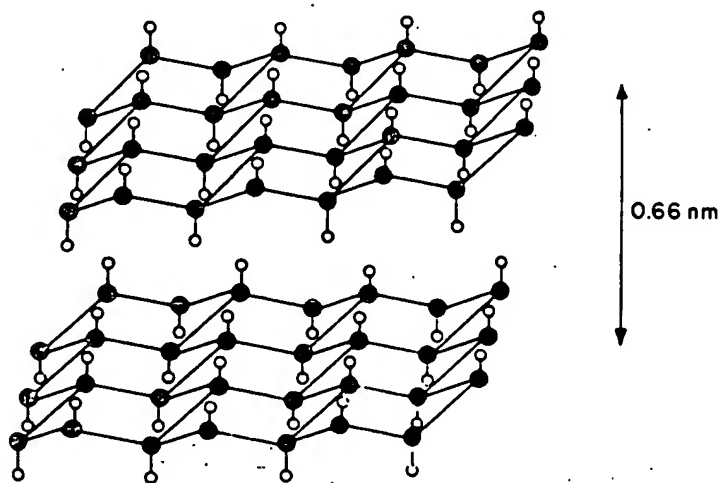


Figure 1. Structure of poly(carbon monofluoride). ●, carbon; ○, fluorine. The interstitial space is 0.66 nm.

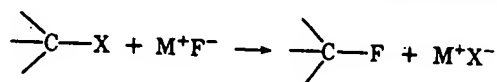
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Until 1970 the direct use of elemental fluorine was usually considered as the classical method of fluorination (12-13), whereas other approaches were regarded as modern methods. It was generally believed that, since the reaction of elemental fluorine with hydrocarbons is highly exothermic, the carbon-carbon bonds are first ruptured, creating free radicals and eventually leading to polymerization. Therefore, in most instances the expected product was a complex mixture of polymers and degradation products, including pure carbon and various fragments of the original hydrocarbon material.

During the last decade researchers have developed diverse fluorination methods which avoid these problems by using certain metal fluorides, inorganic fluorides, or halogen fluorides and electrochemical or indirect methods using certain fluorides as reagents. Hydrogen fluoride has been successfully used as a fluorinating agent and is, in fact, the most widely used industrial fluorinating agent at present.

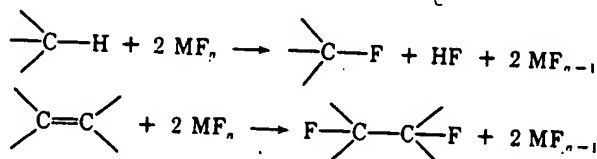
Fluorination of organic compounds using high-valency metallic fluorides (14) can take two forms:

(1) Exchange of halogen with fluorine of the metal fluorides, MF_n :



where $n = \text{Cl, Br, or I}$ and $M = \text{K, Sb, Ag, Hg}_2, \text{ or Hg}$.

(2) Replacement of hydrogen with the fluorine of metal fluorides and addition to double bonds:



High-valency metallic fluorides are very reactive compounds and most decompose in water. They are excellent reagents for fluorination of organic compounds and include CoF_3 , AgF_2 , MnF_3 , CeF_4 , PbF_4 , and possibly BiF_5 and UF_6 . At elevated temperatures, usually 100-400°C, they react with organic compounds producing the fluoro derivatives and the corresponding lower fluorides such as CoF_2 and AgF . Using cobalt trifluoride at up to 400°C, all hydrogen atoms of a hydrocarbon can be replaced by fluorine if the product is thermally stable. Similar addition of fluorine to unsaturated linkages and to aromatic nuclei takes place. These reactions are carried out with organic compounds either in the liquid or in the vapor state. When the organic compound is a liquid, the fluorinating agent (metal fluoride) is added to the heated sample with stirring. In some cases, the organic compound may be suspended or dissolved in an inert solvent, usually a high boiling fluorocarbon. In vapor-phase fluorination, a stream of the organic compound is swept over a bed of fluoride in a heated reactor. In general, fluorination has been more successful in the vapor phase than the liquid phase but yields tend to be low and extensive thermal degradation occurs at high temperatures.

Kinetic as well as thermodynamic problems are encountered in fluorination. The rate of reaction must be decelerated so that the energy liberated may be absorbed or carried away without degrading the molecular structure. A significant recent advance in direct fluorination is the La-Mar process (15-17).

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Thermochemistry

Thermodynamic considerations are of utmost importance in fluorinations. Table 1 is based on JANAF data (18) for CH_4 , which indicate an average carbon—hydrogen bond strength of 410.0 kJ/mol (98 kcal/mol) based on the atomization energy of CH_4 . Table 2 is based on JANAF data for tetrafluoroethylene. This is, perhaps, a poor choice since the double bond in C_2F_4 is extremely weak. Reliable enthalpies and free energy functions for the average double bond are only available at 25°C.

The limiting parameter to be considered in attempting to develop a satisfactory method for controlling reactions of elemental fluorine is the weakest bond in the reactant compound. For hydrocarbons the average carbon—carbon single bond strength is 351.5–368.2 kJ/mol (84–88 kcal/mol). The overall reaction for the replacement of hydrogen by fluorine is exothermic enough [$\Delta G_{25} = -432.6$ kJ/mol (-103.4 kcal/mol)] for a fracture of carbon—carbon bonds if it were to occur via a concerted mechanism or on several adjacent carbon atoms simultaneously. This energy must be dissipated so as to avoid the fragmentation of the molecular skeleton. The comparison of 359.8 kJ/mol (86 kcal/mol) vs 430.9 kJ/mol (103 kcal/mol) has been cited in many previous discussions as an obvious basis to predict the failure of direct fluorination methods. For the rapid reaction rates, which were employed in most previous experiments, this is a valid argument.

It can be seen from Table 1 that there are no individual steps that are exothermic enough to break carbon—carbon bonds except the termination step 3a of -407.9 kJ/mol (-97.5 kcal/mol). Consequently, procedures or conditions are desirable that reduce the atomic fluorine concentration or decrease the mobility of hydrocarbon radical intermediates, and/or keep them in the solid state during reaction. It is necessary to reduce the reaction rate to the extent that these hydrocarbon radical intermediates have longer lifetimes permitting the advantages of fluorination in individual steps to be achieved experimentally. It has been demonstrated by epr (electron paramagnetic resonance) methods (19) that, with high fluorine dilution, various radicals do indeed have appreciable lifetimes.

The two possible initiation steps for the free-radical reaction are step 1b, and the combination of steps 1a and 2a from Table 1. The role of initiation step 1b in the reaction scheme is an important consideration in minimizing the concentration of atomic fluorine (20).

As indicated in Table 1, this process could be spontaneous at room temperature [$\Delta G_{25} = -24.4$ kJ/mol (-5.84 kcal/mol)] although the enthalpy is slightly positive.

Table 1. Thermodynamic Data^a for Fluorination of CH_4 , kJ/mol^b

Step	Reaction	ΔH_{25}	ΔH_{325}	ΔG_{25}	ΔG_{325}
initiation 1a	$\text{F}_2 \rightarrow 2 \text{F} \cdot$	157.7	161.0	123.6	87.4
1b	$\text{F}_2 + \text{RH} \rightarrow \text{R} \cdot + \text{HF} + \text{F} \cdot$	16.3	21.3	-24.4	-79.1
propagation 2a	$\text{RH} + \text{F} \cdot \rightarrow \text{R} \cdot + \text{HF}$	-141.4	-139.7	-151.2	-156.9
2b	$\text{R} \cdot + \text{F}_2 \rightarrow \text{RF} + \text{F} \cdot$	-25.5	-290.8	-284.9	-268.4
termination 3a	$\text{R} \cdot + \text{F} \cdot \rightarrow \text{RF}$	-446.8	451.8	-407.9	-356.0
3b	$\text{R} \cdot + \text{R} \cdot \rightarrow \text{R}-\text{R}$	-350.6	-347.5	-294.1	-240.6
overall reaction	$\text{RH} + \text{F}_2 \rightarrow \text{RF} + \text{HF}$	-430.5	-430.5	-432.6	-430.9

^a Based on JANAF table data (18).

^b To convert J to cal, divide by 4.184.

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68.4
56.0
40.6
30.9

Table 2. Thermodynamic Data^a for Fluorination of Double Bonds, kJ/mol^b

Step	Reaction	ΔH_{25}^a	ΔH_{325}^a	ΔG_{25}^a	ΔG_{325}^a	ΔH_{25}^c	ΔH_{325}^c	ΔG_{25}^d	ΔG_{325}^d	ΔH_{25}^e
initiation 4a	$F_2 \rightarrow 2 F\cdot$	157.7	161.0	123.5	87.4	-157.7				
4b	$R_2C=CR_2 + F_2 \rightarrow R_2C\cdot FCR_2 + F\cdot$	-156.9	-150.2	-151.0	-145.6	35.5	-75.1	-75.3	-72.8	17.8
initiation and termination 5	$R_2C=CR_2 + F_2 \rightarrow R_2CF\cdot FCR_2$	-674.8	-674.5	-624.2	-572.3	-515.9	-337.4	-336.8	-312.1	-258.0
propagation 6a	$R_2C=CR_2 + F\cdot \rightarrow R_2C\cdot FCR_2$	-314.6	-311.3	-274.5	-235.6	-194.6	-157.3	-155.6	-135.1	-118.0
6b	$\cdot CR_2\cdot CFR_2 + F_2 \rightarrow R_2CF\cdot FCR_2 + F\cdot$	-359.8	-362.7	-349.4	-336.4	-290.0	-179.9	-181.6	-174.9	-145.0
termination 7a	$F\cdot + \cdot CR_2\cdot FCR_2 \rightarrow R_2CF\cdot FCR_2$	-684.9	-524.2	-473.2	-424.2	-447.7	-259.0	-261.9	-236.4	-223.8
7b	$F\cdot + F\cdot \rightarrow F_2$	-157.7	-161.0	-123.5	-87.4	-157.7				
7c	$\cdot CR_2\cdot FCR_2 + \cdot CR_2\cdot FCR_2 \rightarrow FCR_2CR_2\cdot$					-435.1				
overall reaction	$R_2C=CR_2 + F_2 \rightarrow R_2CF\cdot FCR_2$	-674.8	-674.5	-624.2	-572.4	-515.9	-337.4	-336.8	-312.12	-258.0

^a Based on JANAF table data (18).

^b To convert J to cal, divide by 4.184.

^c Based on bond strengths for average carbon-carbon double bond.

^d Energy per carbon atom based on same data as ^a.

^e Energy per carbon atom based on same data as ^c.

The validity of this step has not yet been conclusively established by spectroscopic methods which makes it an unsolved problem of prime importance. Furthermore, the fact that fluorine reacts at a significant rate with some hydrocarbons in the dark at temperatures below -78°C indicates that step 1b is important and may have very little or no activation energy at RT. At extremely low temperatures (ca 10 K) there is no reaction between gaseous fluorine and CH_4 or C_2H_6 (21).

A simple equilibrium calculation reveals that, at 25°C and atmospheric pressure, fluorine is less than 1% dissociated, whereas at 325°C an estimated 4.6% dissociation of molecular fluorine is calculated. Obviously, less than 1% of the collisions occurring at RT would result in reaction if step 1a were the only important initiation step. At 325°C the fluorine atom initiation step should become more important. From the viewpoint of energy control, as seen in Table 1, it would be advantageous to have step 1b predominate over step 2a and promote attack by molecular rather than atomic fluorine. Ambient or lower temperatures keep the atomic fluorine concentration low.

In the addition of fluorine to double bonds (see Table 2), the energetic situation is less severe, ie, the addition of fluorine to double bonds is only 251.4–292.9 kJ/mol (60–70 kcal/mol) exothermic per carbon—carbon bond. This energy is not sufficient to fracture the carbon skeleton if care is taken to keep addition from occurring on several adjacent carbon atoms simultaneously. Here, as in the case of hydrogen removal, the individual steps are less exothermic than the overall reaction. It has been established experimentally that less fragmentation occurs and, correspondingly, a higher yield is obtained with most conventional fluorination processes when an unsaturated rather than a saturated hydrocarbon is the starting material. This is owing to the greater exothermicity of the reaction with hydrogen, ie, 434.7 kJ/mol (103.9 kcal/mol) per saturated carbon atom as compared with 207–289.8 kJ/mol (50–70 kcal/mol) per unsaturated carbon atom. In the case of addition of fluorine to double bonds (see Table 2), the corresponding initiation step 4b, is probably exothermic by 20.7–190.4 kJ/mol (5–46 kcal/mol) and thus plays an important role. A second important possibility is the concerted mechanism of step 5 which is exothermic by 207.0–283.2 kJ/mol (50–58.4 kcal/mol) per carbon atom.

Steric Factors

Initially, most of the collisions of fluorine molecules with saturated or aromatic hydrocarbons occur at a hydrogen site or at a π -bond (unsaturated) site. When collision occurs at the π -bond, the double bond disappears but the single bond remains because the energy released in step 4b (Table 2) is insufficient to fracture the carbon—carbon single bond. Once carbon—fluorine bonds have begun to form on the carbon skeleton of either an unsaturated or alkane system, the carbon skeleton is somewhat sterically protected by the sheath of fluorine atoms. Figure 2, which shows the crowded helical arrangement of fluorine around the carbon backbone of polytetrafluoroethylene (PTFE), is an example of an extreme case of steric protection of carbon—carbon bonds (22).

The nonbonding electron clouds of the attached fluorine atoms tend to repel the oncoming fluorine molecules as they approach the carbon skeleton. This reduces the number of effective collisions, making it possible to increase the total number of collisions and still not accelerate the reaction rate as the reaction proceeds toward com-

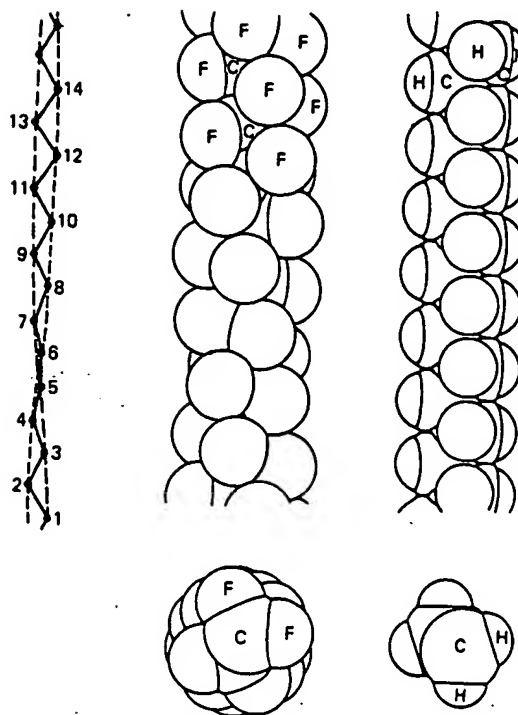


Figure 2. Models of polytetrafluoroethylene and polyethylene chains showing the protective effect of fluorine on the carbon—carbon bond.

pletion. This protective sheath of fluorine atoms provides the inertness of Teflon and other fluorocarbons. It also explains the fact that greater success in direct fluorination processes has been reported when the hydrocarbon to be fluorinated had already been partially fluorinated by some other process or was prechlorinated, i.e., the protective sheath of halogens reduced the number of reactive collisions and allowed reactions to occur without excessive cleavage of carbon—carbon bonds or runaway exothermic processes.

Kinetic Control of the Rate of Elemental Fluorine Reaction.

In direct fluorination processes, concentration, time, and temperature can be controlled. In most previous work, the fluorine was diluted with an inert gas such as nitrogen, helium, or even carbon dioxide. However, the concentration of fluorine in the reactor was kept at a constant level, usually 10% or greater, by premixing the inert gas with fluorine in the desired proportion and then introducing this mixture into the reactor. The rate of reaction between a hydrocarbon compound and a 10% fluorine mixture is relatively high and this very exothermic process can lead to fragmentation (see Table 3) and, in some cases, to combustion. The initial stages of reaction are most critical and nearly all the fragmentation occurs at this time. An initial concentration of 10% fluorine or more is, for most compounds, much too high for nondestructive fluorination.

Molecular relaxation processes such as vibrational or rotational relaxations or

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Table 3. Thermodynamic Data^a for Fluorination of C₂H₆ in kJ^b per Carbon Atom Fragment

Step	Reaction	ΔH_{25}	ΔH_{325}	ΔG_{25}	ΔG_{325}
1	$\text{H}_3\text{C}-\text{CH}_3 + \text{F}_2 \rightarrow 2 \text{H}_3\text{CF}$	-266.1	-268.2	-264.4	-261.5
2	$\text{H}_3\text{C}-\text{CH}_3 + 2 \text{F} \cdot \rightarrow 2 \text{H}_3\text{CF}$	-344.8	-348.5	-329.5	-305.4

^a Based on JANAF table data (18).^b To convert J to cal, divide by 4.184.

thermal conduction make it possible to dissipate the energy released during fluorination. Such relaxation processes are capable of minimizing the chances that the energy required to break the weakest bond is appropriately localized if the reaction sites are widely distributed over the system. Therefore, in the initial stages of fluorination it is necessary to reduce the probability of adjacent reaction sites simultaneously occurring in the same molecule, or in adjacent molecules in a crystal, by diluting the reactants and relying on relaxation processes to distribute the energy over the entire system and thus avoid fragmentation.

A very low initial fluorine concentration is used in the La-Mar fluorination process (17). Initially, the reactor is passivated with helium or nitrogen and fluorine is then fed slowly into the system. If pure fluorine at low pressure is the incoming gas, the fluorine pressure may approach one atmosphere over an extended time period. The very low concentrations of fluorine in the system greatly decrease the probability of simultaneous fluorine collisions on the same molecule or on adjacent reaction sites. As previously discussed, reactant molecules are able to withstand more fluorine collisions, as they become more highly fluorinated, without decomposition because some sites are sterically protected, ie, collisions at carbon-fluorine sites are obviously nonreactive. The fluorine concentration may therefore be increased as the reaction proceeds to obtain a practical reaction rate. Actual dilution schemes to achieve successful fluorination must be individually tailored for specific reaction systems and may, in some cases, include a stepwise procedure.

Thus, for a successful fluorination process involving elemental fluorine, the number of collisions must be drastically reduced in the initial stages; the rate of fluorination must be slow enough to allow relaxation processes to occur and a heat sink must be provided to remove the reaction heat.

Most direct fluorination reactions with organic compounds are performed at or near room temperature unless: (1) reaction rates are so slow that even a fluorine pressure of 101.3 kPa (1 atm) does not lead to appreciable reaction; (2) a vapor-phase reaction is desired and it is necessary to heat the sample being treated to get enough vapor; or (3) reaction rates are so fast that excessive fragmentation, charring or decomposition occurs and a much lower temperature is desirable.

Examples of all three types are known. Thus in the production of partially fluorinated lubricating oils (23) fluorine gas is bubbled at 101 kPa (1 atm) through medium weight oils at 50, 75, and 100°C. For production of fluorocarbon coatings on natural or synthetic rubber or polypropylene, temperatures of 25–50°C are optimum. The fluorination of hot hydrocarbon vapors like gaseous naphthalene or gaseous anthracene (24) is not too satisfactory because fragmentation and charring lead to low yields.

Low temperature fluorination techniques (–78°C) are promising for the preparation of complex fluorinated molecules, especially where functional groups are present (25); eg, fluorination of hexamethylethane to perfluorohexamethylethane, of nor-

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bornane to perfluoro- and 1-hydroxypentadecafluoronorbornane, and of adamantane to 1-hydroxypentadecafluoroadamantane.

Extremely low temperatures have been used to moderate the reactivity of fluorine still further. Hydrocarbons such as methane, ethane, ethylene, allene, benzene, or acetylene, can be co-condensed into a solid fluorine matrix at 20 K without reaction (26-27). This has permitted the study of the reactivity of molecular fluorine without monatomic free-radical chain reactions. Atom reactions can be initiated by uv photolysis.

Infrared absorption spectroscopy provides a convenient method of monitoring these reactions. Ethylene and propylene are particularly interesting since they can be kept indefinitely in solid fluorine in the dark but when exposed to near ir radiation, 1-2 μ m, fluorine is added across the double bond. Ethylene gives the less stable trans conformer of 1,2-difluoroethane. Under identical conditions propylene reacts more rapidly which suggests that the presence of a methyl group has an accelerating effect. Further fluorination studies of ethylene show that, when the fluorine is diluted with argon, reaction with a single fluorine molecule leads to fluoroethylene and hydrogen fluoride; thus the double bond is not attacked. As the concentration is increased the production of *trans*-1,2-difluoroethane increases (28). The acceleration by methyl substitution was demonstrated by the reaction of propylene immediately upon condensation with fluorine. This suggests that little or no activation energy barrier exists for reaction of these molecules with molecular fluorine.

Experimental Techniques

In early reaction systems (2-3,29-30) the vaporized hydrocarbon was combined with nitrogen in a reactor and mixed with a nitrogen-fluorine mixture from a preheated source. The jet reactor (4) for low molecular weight fluorocarbons was an important improvement. The process takes place at around 200-300°C, and fluorination is carried out in the vapor state.

At 200-300°C many compounds, both organic and inorganic, are marginally stable, and certainly not in their lowest vibrational states. They may even undergo some pyrolytic decomposition. Thus the addition of extra energy produced by the interaction of fluorine with these compounds is likely to produce substantial fragmentation. Vaporization of high molecular weight hydrocarbons is rather difficult, and their fluorination was not attempted in the earlier pioneering studies.

The typical fluorination apparatus used for these reactions is simple in design (see Fig. 3) (31). It is essential that the materials of construction are resistant to fluorine (see Table 4) (32). The presence of even traces of oxygen or moisture can have a deleterious effect and, therefore, extreme precautions must be taken to eliminate these contaminants.

The connections are conveniently made of 0.635 cm OD copper tubing. When the fluorocarbon produced in the reaction is volatile, a cold finger-type trap can be placed between the reaction chamber and the trap to catch volatile products. The temperature of the trap must be high enough to pass unreacted or excess fluorine and nitrogen but cold enough to condense the reaction products. Before the reaction is started, the whole system is purged with helium or nitrogen for ca 30 min, and then 0.5-2 mL of fluorine and 50-100 mL of nitrogen per minute are passed through the system. Solid material has to be ground to a very fine powder to achieve complete fluorination.

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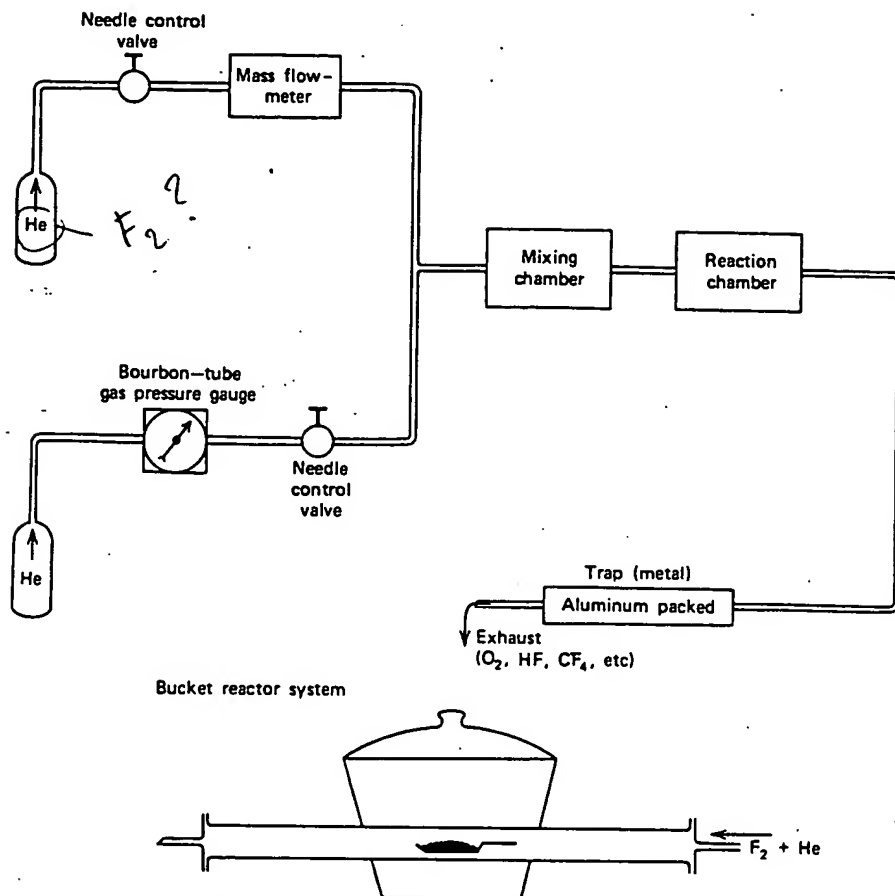


Figure 3. Diagram of typical fluorination apparatus.

A special cryogenic reactor (33) in which the reactions of fluorine with liquid and gaseous samples can be controlled at very low temperatures is shown in Figure 4. Reactants are volatilized into the reaction zone of the cryogenic reactor from the heated oil evaporator prior to initiation of the reaction. The main reaction chamber is a nickel tube, 2.54 cm in diameter, packed with copper turnings. The compartments (10.1 × 10.1 × 20.2 cm) are constructed of stainless steel and insulated with urethane foam and act as heat sinks. All connections are made of 0.635 cm copper or aluminum tubing. A sodium fluoride trap is used to remove the hydrogen fluoride from the reaction products. By cooling or warming the compartments, they can be used to create a temperature gradient along the reaction tube. As the products are highly fluorinated, they are usually volatile and tend to move through the reactor tube rapidly, depending on the temperature gradient. This provides a continually renewed surface of reactant at the optimum temperature for fluorination. Fluorinated copper turnings effectively increase the surface area of the compound exposed to fluorine. The individual zones of the reactor may be cooled with various solvent-liquid nitrogen slushes. Preferably, the temperature is precisely regulated with an automatic liquid nitrogen temperature controller. In addition to the four-zone reactor shown in Figure 4, a multizone reactor can also be used; an eight-zone reactor has been found to be particularly efficient (34). Internal Freon cooling is very effective for controlling the temperatures of the various compartments (35).

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Table 4. Materials Resistant to Dry^a Fluorine

Temperature, °C	Fluorine-resistant materials ^b	
25-150	carbon (graphite, diamond) magnesium and its alloys iron and its alloys nickel and its alloys copper and its alloys metal oxides CaF ₂ , LaF ₃ , LaB ₆	polyethylene polypropylene rubber polystyrene poly(vinyl chloride) Teflon Kel-F
up to 500	copper nickel Monel carbon (graphite, diamond) nickel-aluminum alloys carbon (diamond) Al ₂ O ₃ , UO ₂ , ThO ₂	metal oxides CaF ₂ LaF ₃ LaB ₆ CaF ₂ , LaF ₃ LaB ₆
up to 1000-1500		

At 2000°C carbon and other refractory metals react slowly to form gaseous mono- or difluorides and other species; refractory oxides form volatile fluorides + O₂; refractory carbides form metal fluorides + CF₄; etc.

^a Moisture results in HF development and increased corrosion of metals.

^b Protection of fluoride or fluorocarbon film.

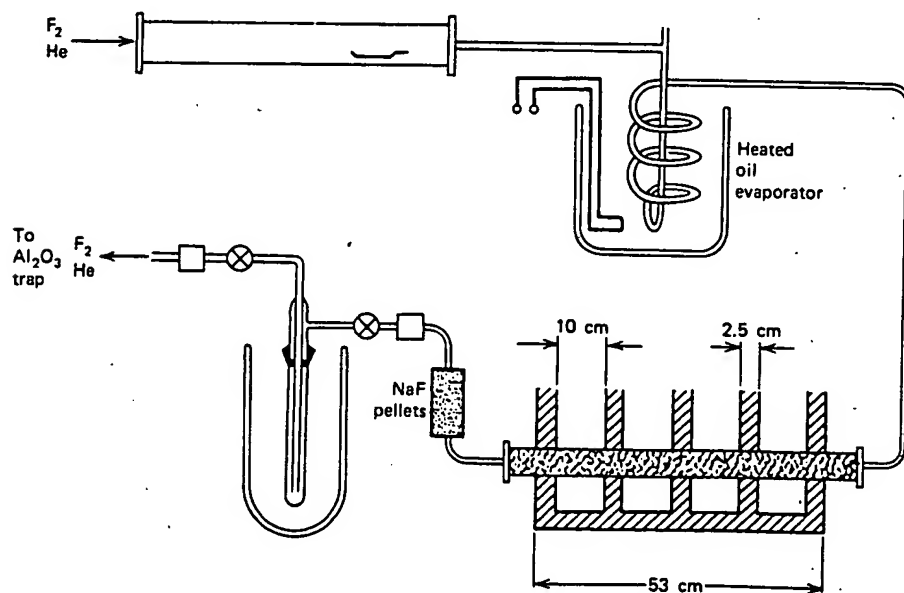


Figure 4. Cryogenic reactor system.

Oxygen or moisture has to be excluded because the presence of oxygen leads to cross-linking, presumably with epoxy bridges, to carbonyl groups which give acid fluorides, and to peroxides (36). Cross-linking obviously decreases the yield of pure perfluorocarbon. It can be detected by its activity in the 1600-2000 cm⁻¹ region and by noting the polymeric nature of the products, ie, high melting points, low vapor pressures, etc.

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Applications

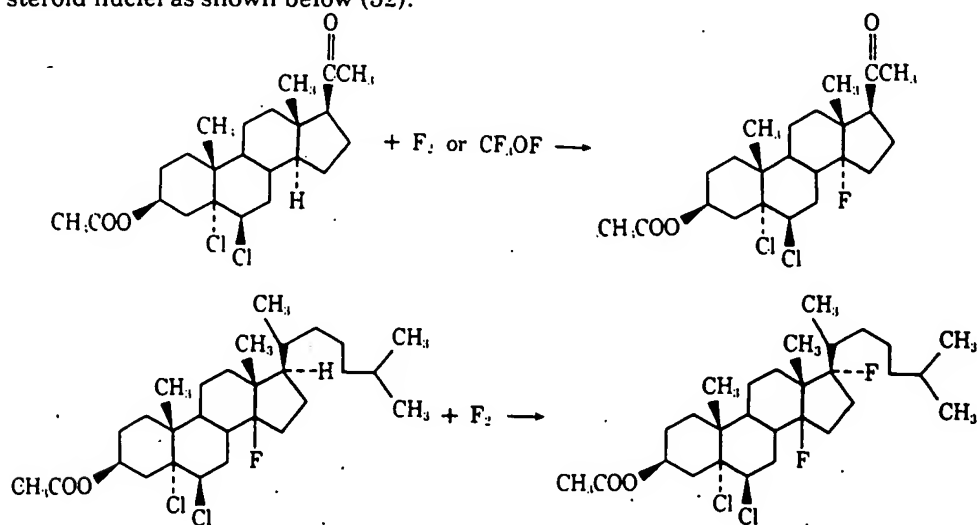
Direct fluorination, though it sometimes leads to degradation, cross-linking, and combustion can be controlled and useful products derived (37). Even though direct fluorination sometimes produces a very low yield of desired products, it may offer the only possible method of preparation. Oxyfluorination is a new technique (38) offering unique possibilities for the functionalization of fluorocarbons and for the preparation of fluoromembranes.

In 1954 the surface fluorination of polyethylene sheets by using a water-cooled heat sink was patented (39). Later patents covered the fluorination of PVC (40) and of polyethylene bottles (41). Studies of surface fluorination have been reported (42). The fluorination of polyethylene powder was described (24) as a fiery intense reaction, which was finally controlled by dilution with an inert gas at reduced pressures. Direct fluorination of polymers was achieved by Lagow and Margrave in 1970 (11,43). More recently, surface fluorinations of poly(vinyl fluoride), polycarbonates, polystyrene, and poly(methyl methacrylate), and the surface fluorination of containers have been described (44-45). Partially fluorinated poly(ethylene terephthalate) and polyamides like nylon have good soil release properties as well as high wettability (46-47).

The following companies manufacture organic fluorine compounds by direct fluorination techniques: Air Products and Chemicals, Inc., Tamaqua, Pa.; MarChem, Inc., Houston, Tex.; Ozark-Mahoning, Inc., Tulsa, Okla.; and PCR, Inc., Gainesville, Fla.

Simple and Complex Organic Molecules. A great variety of new perfluoro and partially fluorinated compounds has been synthesized (48-54). The direct fluorination of CS_2 (49) has produced several derivatives including SF_5CF_3 , $(\text{SF}_3)_2\text{CF}_2$, $\text{SF}_5\text{CF}_2\text{SF}_3$, SF_3CF_3 and $\text{F}_3\text{SCF}_2\text{SF}_3$; and the treatment of $\text{Si}(\text{CH}_3)_4$ or $\text{Ge}(\text{CH}_3)_4$ with F_2 (50) can produce most of the Si-C-H-F or Ge-C-H-F species possible. The fluorination of $\text{Hg}(\text{CH}_3)_2$ yields $\text{Hg}(\text{CF}_3)_2$. In all these cases, the identities of the products have been confirmed by elemental analyses, and ir, mass, and nmr spectra. Low temperature fluorination methods (33,48-50) lead to high yields of acid fluorides (55), perfluoroethers (56), and other functionalized organic species (57).

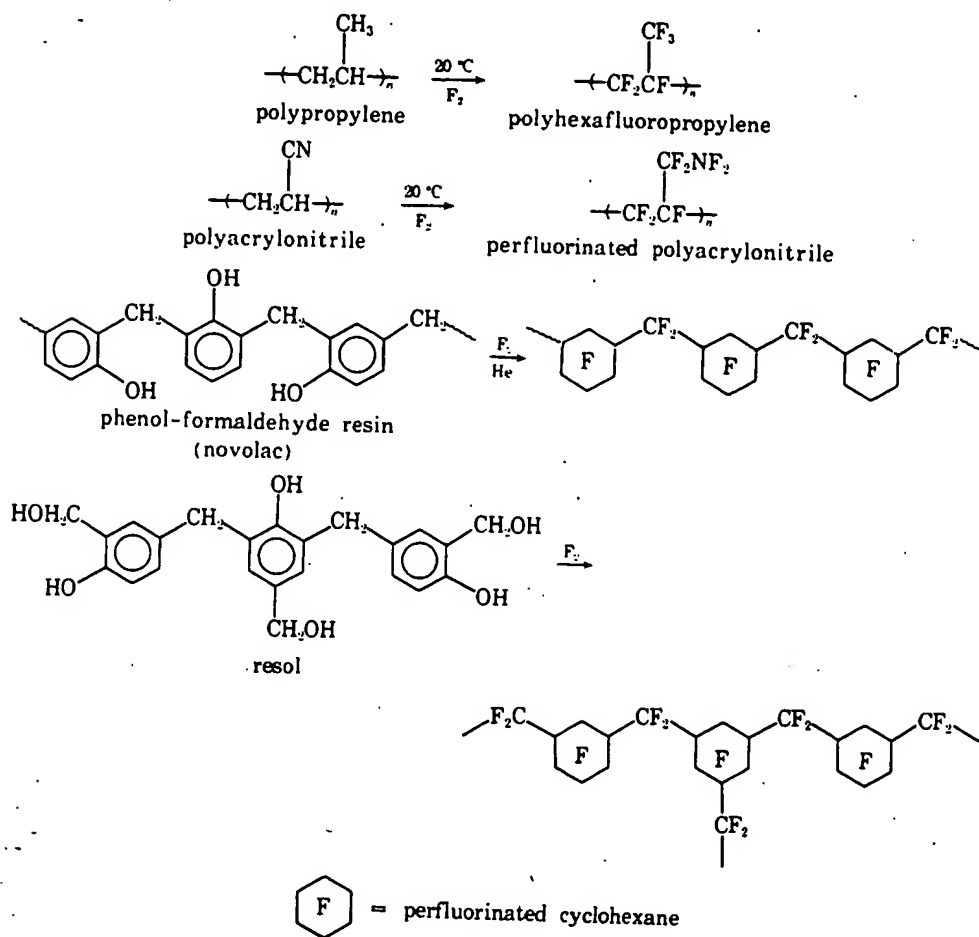
Direct electrophilic fluorination (52) of adamantane gives fluoroadamantane. Elemental F_2 was used for the selective functionalization of carbons-14 and 17 of the steroid nuclei as shown below (52):



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Furthermore, 5-fluorouracil can be prepared directly by low temperature fluorination of a Freon-uracil slurry (53).

Hydrocarbon Polymers. It is difficult to produce perfluorocarbon polymers by the usual methods. Many monomers, such as hexafluoropropylene, polymerize only slowly because of the steric hindrance of fluorine. Furthermore, some monomers are not very stable and are difficult to synthesize. Direct fluorination can be used for the direct synthesis of fluorocarbon polymers (58) and for producing fluorocarbon coatings on the surfaces of hydrocarbon polymers (11,31,39-43,58-59). Some hydrocarbon polymers and their hypothetical fluorocarbon perfluoro-analogues are shown below:



Thus fluorocarbon polymers can be produced with chemical compositions very similar to polytetrafluoroethylene by the direct reaction of fluorine with polyethylene and the perfluoro analogues of polypropylene and polystyrene can be prepared. These fluorocarbon polymers differ from the more familiar linear structures because carbon-carbon cross-linking occurs to a significant extent during fluorination. Most of these fluoropolymers are white solids with high thermal stability; some are stable in air as much as 200°C above the ignition temperatures of their corresponding hydro-

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carbon precursors. Hydrocarbon polymers such as polyethylene and the new surfaces formed by direct fluorination have been studied by esca which shows that the surface is truly converted to a fluorocarbon polymer (60) (see Analytical methods). Most of these fluorocarbon surfaces are inert and many of them have good lubricant properties. The fluorination of PVC has been followed with esca and $(CF_x)_n$ polymer was also identified (61).

If solid polymers or polymer particles larger than ca 100 μm are fluorinated, only surface fluorination results. Penetration of fluorine and the conversion of hydrocarbon to fluorocarbon can occur to depths of at least 0.1 mm. Fluorocarbon-coated objects should have many practical applications because the chemically adherent surface provides: increased thermal stability; resistance to oxidation and corrosive chemicals and solvents; decreased coefficient of friction, and thus decreased wear; and decreased permeability to gas flow. Unusual surface effects can be obtained by fluorinating the polymer surfaces only partially (62).

Natural and Synthetic Rubber. Fluorination of natural or synthetic rubber creates a fluorocarbon coating (31,63-64) which is very smooth and water-repellent (see Waterproofing). Rubber articles such as surgical gloves, O-rings, gaskets, and windshield wiper blades, can be fluorinated on the surface while the interior retains the elastic, flexible properties of the natural rubber. Fluorinated O-rings can be used without extra lubricant in corrosive atmospheres since the fluorocarbon is unreactive. In food-processing equipment, grease or lubricants are eliminated and do not contaminate the food products. Fluorinated O-rings have smooth surfaces, very low

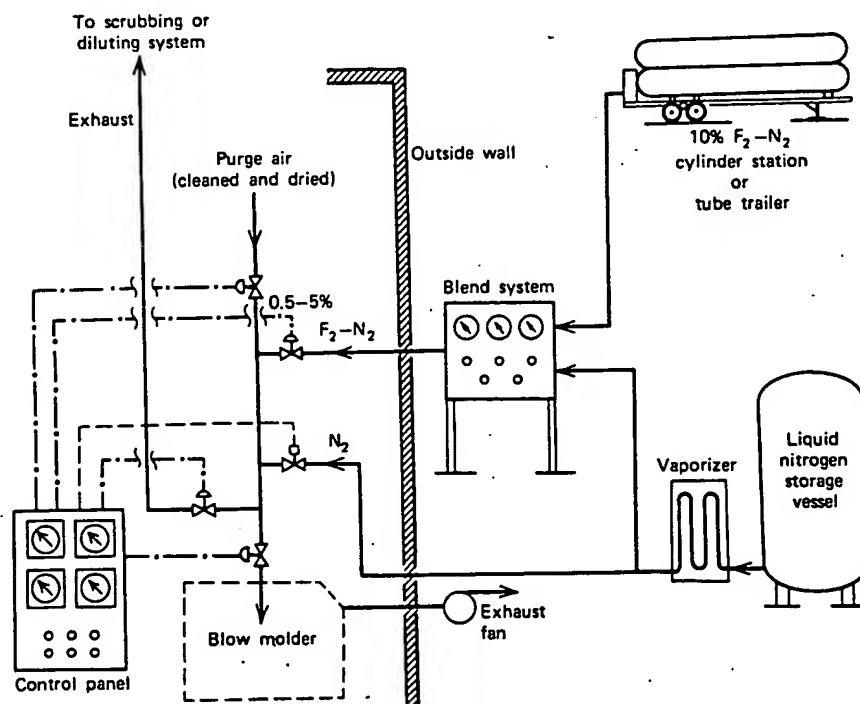


Figure 5. System for the blow molding of polyolefin containers with fluorine-nitrogen mixtures.

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frictional coefficients, and enhanced thermal stabilities. Fluorinated windshield wiper blades have a very low coefficient of friction, run smoother with less squeak, their surface is more resistant to the sun's uv radiation and attack by ozone, and they require less electrical energy for operation.

Many applications of this technique are apparent in medicine, such as surgical rubber gloves, rubber sheets, drain tubes, catheters, etc. Since talcum or other lubricating powder often used with surgical gloves can cause allergic reactions, thin powderless gloves are desirable. Teflon or silicone films have proved unsuccessful for surgical gloves. However, an excellent direct fluorination process has been developed (64) whereby the inside surfaces are fluorinated under expanded conditions at elevated temperatures. A very smooth surface is obtained and powder is not required. At the same time, the outside surface remains rough so that surgical instruments can be held firmly without slippage. The tactile sensitivity of the tips of the fingers seems to be increased, and the problem of powder forming lumps or a mudlike slush inside the glove is eliminated.

Blow-Molded Containers. A surface-fluorination process has been developed for the blow-molding industry to produce solvent-resistant polyolefin containers (see Fig. 5). In this application, the air which is normally used to blow mold containers is replaced by a low concentration of fluorine in nitrogen. Airopak containers produced by this process show outstanding resistance to nonpolar solvents (44-45,65-66) and are being evaluated for use as vehicle fuel tanks.

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